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(54) Title: CONTACT LENS ARTICLES MADE FROM PERFLUORINATED COMONOMERS		
(57) Abstract A rigid, gas-permeable, high-Dk fluoropolymeric contact lens article, including both contact lenses and buttons from which contact lenses is disclosed. More specifically, the subject contact lens article comprises copolymers of certain perfluorinated heterocyclic comonomeric units that provide an improved balance of properties, including high oxygen-transmissibility, necessary for extended-wear or specialty lenses. Such copolymers have been found to be sufficiently rigid for normal lathing and economic manufacture. The contact lenses are biocompatible when surface-treated.		

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CONTACT LENS ARTICLES MADE FROM PERFLUORINATED COMONOMERS

FIELD OF THE INVENTION

Improved contact lens compositions are achieved through incorporation of certain perfluorinated, heterocyclic comonomers in extended-wear or specialty rigid, gas-permeable (RGP) contact lenses. In particular, the present invention is directed toward high-Dk fluoropolymeric contact lenses or precursors thereof, such as the cylindrical buttons from which RGP contact lenses are commonly produced.

BACKGROUND

In general, there are numerous well-known fluoropolymers in the class generally regarded as fluoroplastics, including amorphous fluoropolymers exhibiting optical transparency. Commonly, these conventional polymers have been developed to be stable at high temperature and resistant to chemical attack, with the degree of stability and inertness increasing with fluorine content in the molecule. While the physical and chemical properties of known fluoropolymers are highly desirable for many purposes, they are relatively difficult to manufacture and hence relatively expensive compared to other polymer materials. Their inertness makes them an unlikely choice for a biocompatible material. As a consequence, highly fluorinated polymers, especially those containing perfluorinated monomers, would not be a likely candidate for a contact lens to be made by finely controlled lathing and to be worn in the eye for an extended period of time.

Resnick in U.S. Pat. No. 3,978,030 describes certain polymers of perfluoro-2,2-dimethyl-1,3-dioxole (hereafter "PDD"), including both homopolymers of PDD and crystalline copolymers of tetrafluoroethylene (TFE), the latter exemplified with a melting point T_m of about 265° C. The PDD homopolymer is amorphous and has a very high glass transition temperature T_g of about 355° C. The homopolymer is brittle and difficult to fabricate into final products because of poor melt flow and low solubility in available solvents.

Squire in U.S. Pat No. 4,530,569 describes amorphous copolymers of PDD with TFE as well as terpolymers of PDD with TFE and another comonomer. In U.S. Pat Nos. 4,935,477 and 4,754,009, Squire describes copolymers and terpolymers of PDD with comonomers that include certain perfluoroolefins and perfluoro(alkyl vinyl) ethers. It is shown in these patents that, in general, the T_g of those copolymers decreases with increasing comonomer content. For a copolymer containing 10 mol percent of TFE, T_g is decreased to about 260° C. Generally, if the PDD content of those copolymers is less than about 12 mol percent, those copolymers have some crystallinity which is known to adversely affect optical transparency.

The amorphous copolymers of PDD and TFE (commercially available from DuPont under the trademark Teflon® AF) have certain properties that provide them with potential in a number of applications. Representative examples include, in the electronics field, high-density integrated circuits (dielectric layers), packaging material, passivation coatings, encapsulation, and lithography; in the optical field, lens covers, optical fibers, coatings, UV-transmission devices, radar devices, and anti-reflective coatings; in the biomedical field, thin film membranes, biocompatible coatings, optical sensors, and integrated optics; and in the chemical industry, protective coatings, process sight glass, high-performance parts and non-stick surface-releasing agents.

U.S. Patent 5,147,417 to Nemser discloses a membrane formed from an amorphous polymer of PDD (perfluoro-2,2-dimethyl-1,3-dioxole), the membrane exhibiting an oxygen-nitrogen selectivity of at least 1.4:1. The membrane is part of an automotive air intake system for a mobile combustion engine. The membrane preferably has an oxygen flux in excess of 100 Barrers, especially in excess of 500 Barrers. The air intake system provides either oxygen-enriched air or oxygen-depleted air for the engine, depending on the mode of operation of the engine.

In particular regard to contact lenses, rigid-gas-permeable, i.e., "RGP" contact lenses have been available for many years. Previously, high-Dk RGP materials have been commercially made from silicone-containing monomers such as disclosed in U.S. Patent Nos. 4,152,508; 4,330,383; 4,686,267; 4,826,889; 4,826,936; 4,861,850; 4,996,275; and 5,346,976. The art has recognized that introducing fluorine-containing groups into contact lens polymers can increase oxygen-permeability. For example, U.S.

Patent No. 4,996,275 to Ellis, et al. discloses using a mixture of comonomers including the fluorinated compound bis(1,1,1,1,3,3,3-hexafluoro-2-propyl)itaconate in combination with organosiloxane components. The fluorination of certain monomers used in the formation of silicone hydrogels has been indicated to reduce the accumulation of deposits on contact lenses made therefrom, as described in U.S. Patent Nos. 4,954,587; 5,079,319 and 5,010,141. Moreover, the use of silicone-containing monomers having certain fluorinated side groups, i.e., $-(CF_2)_n-H$, has been found to improve compatibility between the hydrophilic and silicone-containing monomeric units, as described in U.S. Patent Nos. 5,387,662 and 5,321,108.

Although there have been some attempts to develop a highly-fluorinated material for contact lenses, such attempts have had limited success. Contact lens compositions based on fluoroalkylacrylates are known in the art. These materials range from soft to semi-rigid and often require the use of special wetting agents or surface treatments. Contact lenses based on telechelic perfluorinated polyethers are disclosed in US Patent No. 4,818,801 to Rice et al. Although having high oxygen permeability and resistance to absorption of tear components, they can be relatively soft, making it difficult to use conventional machining techniques known in the art.

U.S. Patent No. 3,389,012 to Hamm discloses a contact lens characterized by a modified edge portion surrounding a centrally located optical portion. The modification of the lens comprises a coating formed on the interior surface of the lens in the edge portion thereof, which coating comprises a tetrafluoroethylene polymer, specifically a Teflon® (TFE) coating.

U.S. Patent No. Re 29,299 to Girard et al. and US Patent No. 3,944,347 discloses contact lens made from copolymers and terpolymers of perfluoro-2-methylene-4-methyl-1,3-dioxlane, referred to as PMD. The copolymers of PMD and tetrafluoroethylene provide materials which are said to be especially suitable in that they exhibit refractive indices in the desired range, are characterized by good clarity and an absence of color and haze; further, they exhibit good hardness properties and permeability to oxygen and carbon dioxide, thus increasing the nutrition of the cornea. In particular, Girard et al. disclose that a copolymer containing 92 parts by weight of tetrafluoroethylene with eight parts by weight of PMD is characterized by an index of refraction of 1.349, a Knoop

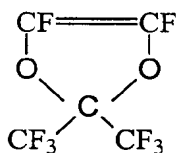
hardness of 4.9, and a molding temperature of 350°C. The patent states that copolymers of PMD and tetrafluoroethylene are characterized by optimum indices of refraction, since the optimum index, that of human tears, is 1.336. In fact, however, contact lens materials with such a low index of refraction have not been commercialized, because they may be impractical or require thicker lenses to achieve the same refractive correction as lenses with a higher index of refraction. A thicker lens may be less comfortable or negate the improved oxygen-transmissibility of the lens material.

In view of the above, the aforementioned highly fluorinated polymers have not been able to compete with the more economical, more easily designed and manufactured, more biocompatible materials on the market for use in RGP contact lenses. Yet fluoropolymers may be able to provide improved oxygen transmissibility or other desirable properties. New polymers are sought which not only provide improved oxygen transmissibility, but which provide an acceptable and advantageous combination of other contact lens properties, including biocompatibility and a sufficiently high modulus or rigidity, to mask corneal astigmatism, that would allow economic manufacture into the final lens design.

A further object of the invention is to provide an ophthalmic lens capable of extended, continuous wear periods of at least 24 hours without substantial adverse impact on the cornea, and more preferably, to provide a lens capable of continuous wear for about one week to about thirty days or more without unacceptable corneal swelling or other adverse effects.

SUMMARY OF THE INVENTION

The present invention involves a high-Dk, fluoropolymeric contact lens article, including both contact lenses and the buttons from which contact lenses are produced. More specifically, the subject copolymer for use in a high-Dk, rigid-gas-permeable contact lens is made from certain perfluorinated cyclic monomers. In particular, the subject lens article comprises a composition polymerized from a monomer mix including suitably 20 to 75 mole percent, preferably 30 to 50 mole percent of monomers represented by the following formula (I):



The present invention further includes methods for making the contact lenses from such copolymers and for rendering the surface biocompatible with eye tissue.

An advantage of the subject invention is that the above-described material not only can improve the oxygen transmissibility of the resulting contact lens, but can be injection molded and/or lathed from buttons or other blanks of the molded material.

DETAILED DESCRIPTION OF THE INVENTION

As indicated above, the present invention is related to a high-Dk fluoropolymeric contact lens or a precursor article. The term "article" as used herein is intended to include lenses and buttons or blanks from which contact lenses are produced by lathing. The term "button" as used herein refers to stock material from which lens surfaces are cut by way of a lathe.

The improved contact lens compositions are achieved through incorporation of certain perfluorinated, heterocyclic comonomers in extended-wear or specialty rigid, gas-permeable (RGP) contact lenses. Contact lenses made from such comonomers have been found amenable to lathing for economic manufacture. A highly advantageous combination of high oxygen transmissibility, optical transparency, and acceptable flexural modulus of has been found for forming a contact lens. Although having a relatively low index of refraction, it has been found that lens design results in a sufficiently thin series of lenses. Finally, treatment of the finally-shaped lens has been successfully accomplished to render the surface of the lens wettable and biocompatible in the eye.

The term modulus will be understood to herein refer to the flexural modulus of the material. The RGP material has a relatively high modulus, ranging from about 1000 to 2500, preferably 1200 to 2400 megapascals (MPa). It is more preferable to provide lenses having moduli in the range of about 1400 to about 2200, and most preferably from about 1600 to about 1900 MPa. The modulus of a lens material can have a significant

impact upon lens comfort. Lenses possessing too high a moduli or stiffness will tend to be brittle, whereas lenses possessing too low a moduli or stiffness will have too much lens flexure on the eye, thus not masking astigmatism.

For the purposes of this invention, it will be understood that the term "gas-permeable" refers specifically to the oxygen permeability through the lens from the atmosphere to the cornea. RGP materials applicable to the present invention suitably have an oxygen-permeability (Dk) that is suitably 100 to 1200 Barrers, preferably 200 to 1000 Barrers, more preferably 200 to 500 Barrers. The oxygen-permeability Dk of a lens material does not depend on lens thickness. The oxygen-permeability is the rate at which oxygen will pass through a material. A Barrer is defined as:

$$((\text{cm}^3 \text{ oxygen})(\text{mm})/(\text{cm}^2)(\text{sec})(\text{mm Hg})) \times 10^{-10}$$

$$\text{or, alternatively, } ((\text{cm}^3 \text{ oxygen})(\text{cm})/(\text{cm}^2)(\text{sec})(\text{mm Hg})) \times 10^{-11}$$

The oxygen transmissibility of a lens, as used herein, is the rate at which oxygen will pass through a specific lens. Oxygen transmissibility, Dk/t, is conventionally expressed in units of Barrers/mm, where t is the average thickness of the material (in units of mm) over the area being measured. For example, a lens having a Dk of 90 Barrers (oxygen-permeability barrers) and a thickness of 90 microns (0.090 mm) would have a Dk/t or 100 Barrers/mm (oxygen transmissibility Barrers/mm).

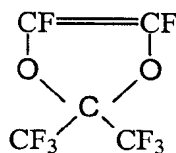
Contact lens materials with high refractive indices (i.e., an index of 1.4 or higher, as for example 1.428, or even 1.5 or greater, as for example, 1.65) are desirable from a lens design standpoint. Additionally, a high refractive index material is preferred when constructing certain types of lenses such as a segmented bifocal lens.

The copolymers of PDD and tetrafluorethylene provide materials that exhibit refractive indices less than 1.40, as for example, in the range of about 1.32. The relatively low refractive index of Teflon AF makes it advantageous for use in cladding for optical fibers in which the greatest difference in refractive index between the cladding and the optical fiber is advantageous for keeping light within the optical fiber. On the other hand, with respect to contact lenses, although an index of refraction of 1.336, that of tears, may be ideal in terms of biocompatibility, higher values are generally used in order to provide the desired refractive lenses with a relatively thin lens. It has been determined, however, that the relatively low refractive index of PDD can, in fact, be

adequately compensated by lens design, for example, a steeper curve in the lens at the anterior surface thereof, such that unduly or disadvantageously thick lenses generally can be avoided. Thus it is possible to produce contact lens according to the invention capable of providing refractive correction with a diopter range of -20.00D to $+20.00\text{D}$.

The contact lens of the invention can be made by a variety of methods known to those skilled in the art, particularly in light of the versatile processability of the perfluorodioxole polymers. These methods include molding into a form such as a rod, button, or other, preferably cylindrical, shape. The copolymer of the present invention, after first being molded and/or cut into a button or the like, can be lathed. It has been found that amorphous copolymers of monomer (I) have the necessary mechanical stability, rigidity/modulus, and response to cutting motion to be lathed, preferably normal or conventional lathing at ambient temperatures. This is important because materials that, on the one hand, are too rubbery, or on the other hand, that are too brittle, are not susceptible to lathing, which in the case of contact lenses must be finely controlled within microns to the necessary dimensional specifications to correct refractive error and comfortably fit the shape of the eye.

As indicated above, it has been found that a new and advantageous contact lens composition can be achieved through the incorporation of the monomer perfluoro-2,2-dimethyl-1,3-dioxole (PDD), which has the following Formula (I):

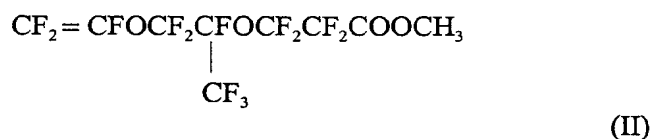


(I)

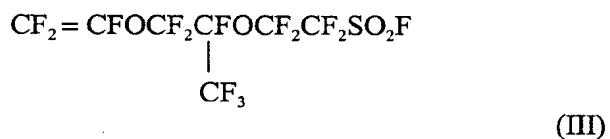
In preferred embodiments, the material of the present invention is polymerized from a monomer mix including 20 to 75 mole percent, and more preferably from about 30 to about 50 mole percent of monomers represented by Formula I. Below 20 mole percent, the composition tends to become cloudy and about 75 mole percent, the modulus tends to become too low for a contact lens. A higher modulus, tending to more resistant to flexing, is necessary to mask an astigmatism of the eye.

A contact lens according to the present invention is formed from an amorphous copolymer that is a generally random copolymer comprising repeat units of PDD with other copolymerizable comonomers, for example, the copolymer can contain units from one or more other fluoromonomers such as tetrafluoroethylene (TFE), hexafluoropropylene, chlorotrifluoroethylene (CTFE), vinylidene fluoride, trifluoroethylene, and perfluoro(alkyl vinyl) ethers (PAVE), having the formula $\text{CF}_2=\text{CFO}(\text{CF}_2\text{CFXO})_n\text{R}_f$, wherein X is F or CF_3 , n is 0-5, and R_f is a perfluoroalkyl group of 1-6 carbon atoms.

Thus, suitable comonomers include but are not limited to perfluoro(alkyl vinyl ethers) such as perfluoro(methyl vinyl ether), perfluoro(ethyl vinyl ether), and perfluoro(*n*-propyl vinyl ether). Other ethers include, for example, methyl perfluoro(3,6-dioxa-4-methyl-8-nonenoate), further referred to as EVE, represented by the following formula:

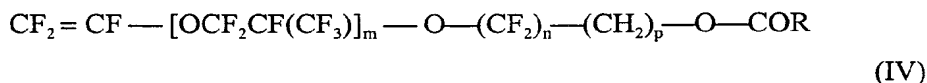


and perfluoro(4-methyl-3,6-dioxa-7-octenyl) sulfonyl fluoride, further referred to as PSEPVE, represented by the following formula:

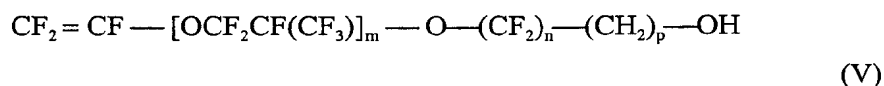


TFE is made in large quantities by E.I. du Pont de Nemours and Company; other suitable representative monomers are available from the following sources: vinylidene difluoride, chlorotrifluoroethylene (CTFE), hexafluoropropylene (HFP), vinyl fluoride, and trifluoroethylene from SCM Specialty Chemicals, Gainesville, Fla.; perfluoro(methyl vinyl ether) (PMVE), and perfluoro(propyl vinyl ether) (PPVE) can be made as described in U.S. Pat. No. 3,1810,8950; (EVE) can be made as described in U.S. Pat. No. 4,138,740; and PSEPVE can be made as described in U.S. Pat. No. 3,282,875. PDD is described in the above-mentioned U.S. Pat. No. 3,978,030.

Other suitable comonomers are functional fluorovinyl ethers having the general formula:

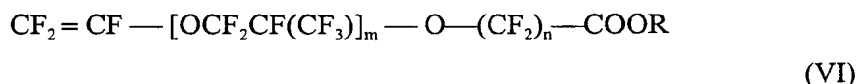


wherein $m=0-20$, $n=1-10$, $p=1-4$ and R is alkyl having 1-6 carbon atoms or phenyl. These monomers can be derived from hydroxy-functional fluorovinyl ethers disclosed in U.S. Pat No. 4,982,009 and having the general formula:



wherein m , n , and p are as defined above. The hydroxy compound (V) can be converted to the ester compound (IV), wherein $R = \text{CH}_3$, by reaction with pyridine, N,N-dimethylaminopyridine, and acetyl chloride in methylene chloride. This reaction can be conducted in glassware, for example, at atmospheric pressure and at cool temperatures such as $0^\circ\text{--}25^\circ\text{C}$, preferably $5^\circ\text{--}15^\circ\text{C}$. The product (IV) can be isolated from the reaction mass by conventional means.

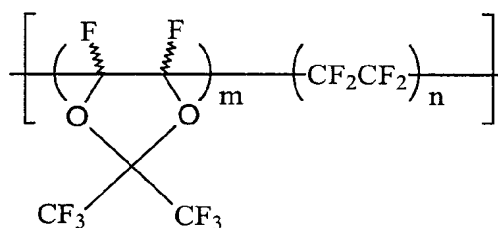
In another embodiment of the invention, the polymers of the invention contain units derived from functional fluorovinyl ether monomers having the general formula:



but which may require post-polymerization esterification because of partial hydrolysis of COOR during aqueous polymerization. The esterification can be carried out by treatment of the polymer; for example, with trimethyl orthoformate.

Carboxylic and sulfonic acid derivatives of the above monomers may also be used to from a copolymerization compatible mixture.

TFE is an especially preferred comonomer, either alone or with other fluoromonomers, especially such a polymer with the above-indicated proportion of perfluoro-2,2-dimethyl-1,3-dioxole. Teflon AF may be represented by the following formula:



Teflon AF

(VII)

The glass transition temperature of Teflon AF depends on its composition: T_g decreases with increasing content of TFE. There are several ways to determine composition of Teflon AF polymers. One of the most convenient is by nuclear resonance (NMR) spectra of the polymer melt. The polymer is sealed in a NMR tube and heated up gradually until it melts, which gives a spectrum with good peak resolution. The monomer ratio is then calculated by peak integration.

The polymer properties of Teflon AF such as high gas-permeability, low refractive index, and low density suggest the presence of "microvoids," or considerable free volume in the Teflon AF polymer structure. This has been substantiated by position annihilation lifetime experiments.

The amorphous polymer preferably has a glass transition temperature of at least 110° C., and more preferably at least 140°C. Glass transition temperature (T_g) is known in the art and is the temperature at which the polymer changes from a brittle, vitreous or glassy state to a rubbery or plastic state. Examples of such copolymers are described in further detail in the U.S. Pat. No. 4,754,009 to Squire.

The glass transition temperature of the amorphous polymer will vary with the actual polymer, especially the amount of tetrafluoroethylene or other comonomers that may be present. Examples of T_g are shown in FIG. 1 of the aforementioned U.S. Pat. No. 4,754,009 to Squire as ranging from about 260° C for copolymers with tetrafluoroethylene having low amounts of tetrafluoroethylene comonomer, down to less than 100° C for the copolymers containing at least 60 mole % of tetrafluoroethylene. The addition of other comonomers may also function to decrease T_g or to provide other desirable properties, such as modulus or hydrophilicity to increase surface wetting.

In order to provide a good mechanical stability, it is believed necessary for the polymeric composition to have a glass transition temperature (T_g) of greater than about 100°C, preferably less than about 160°C, and more preferably between about 100°C and 140°C.

The perfluoropolymers of the present invention can be processed by several methods. Polymerization can be achieved using free radical polymerization initiators commonly used in polymerizing unsaturated compounds known in the art. Representative polymerization initiators include 2,2-azobis(isobutyronitrile) (AIBN); 2,2'-azobis(2,4-di-methylvaleronitrile) (ADV N); 1,1-azobis(cyanocyclohexane) and 2,2'-azobis(2-methylbutyronitrile). In preferred embodiments, AIBN and ADV N are used together at combined concentrations of 0.01 to 0.4 weight percent, with preferably 0.01 to 0.1 weight percent ADV N and 0.1 to 0.3 weight percent of AIBN.

The polymers are melt-processable by conventional methods such as extrusion or compression molding and injection molding can be used to fabricate polymers into shaped articles. The processing temperature is usually about 100° C above the polymer T_g , although longer than usual heating times may be necessary because of their lower thermal conductivities.

Lens buttons prepared by molding or cutting of rods can be processed into the high-Dk fluoropolymeric contact lenses using means well established in the ophthalmic lens arts, including lathing and polishing of the lens surfaces to yield a contact lens of the appropriate thickness. The perfluorodioxole copolymer of the present invention, when made into contact lenses, has good mechanical properties and exhibit the unusually high oxygen-permeability generally associated with the polymer. The gas-permeability increases with the dioxole monomer content, and contact lenses made from the present polymers are characterized, as indicated above, by an oxygen-permeability that is preferably a Dk of about 200 to 1000.

Subsequent to the lathing and other machining operations, the lens is subjected to surface treatment, preferably by means of reductive RF plasma-treatment, employing an hydrogen-containing gas. Plasma-treatment involves passing an electrical discharge through a gas at low pressure. The electrical discharge is usually at radio frequency (typically, 13.56 MHz), although microwave and other frequencies can be used. This

electrical discharge is absorbed by atoms and molecules in their gas state, thus forming a plasma that interacts with the surface of the contact lens. This plasma treatment with hydrogen-containing gas is believed to reduce the fluorine content and increase the carbon content, allowing sites for subsequent oxidation, as proposed in commonly assigned copending application S.N. _____ (docket no. P01565), hereby incorporated by reference in its entirety. Following plasma treatment with hydrogen, the surface is then oxidized by an oxidizing plasma, e.g., employing O₂ (oxygen gas), water, hydrogen peroxide, air, ammonia, etc., or mixtures thereof, creating radicals and oxidized functional groups. Such oxidation renders the surface of a lens more hydrophilic and wettable. Optionally, further surface treatment can be carried out; for example, by the attachment of biocompatible or hydrophilic polymers or macromonomers. In practice, contact lenses may be surface-treated by placing them within an electric glow discharge reaction vessel (e.g., a vacuum chamber). Such reaction vessels are commercially available. The lenses may be supported within the vessel on an aluminum tray (which acts as an electrode) or with other support devices designed to adjust the position of the lenses. The use of specialized support devices which permit the surface treatment of both sides of a lens is known in the art and may be used in the present invention.

In one embodiment of the invention, the plasma treatment with a hydrogen-containing atmosphere is conducted at a wattage of 100 to 1000 watts at a electric discharge frequency of 13.56 MHz, preferably about 200 to 800 watts, and a pressure of 0.1 to 1.0 torr, and the plasma treatment with an oxygen- or nitrogen-containing compound is conducted at a wattage of 25 to 1000 watts and a pressure of 0.1 to 1.0 torr. Preferably, the lens is plasma-treated with hydrogen at 200 to 500 watts for a period of 2 to 20 minutes, and then subsequently plasma treated with air at about 50 to 200 watts for a period of 2 to 20 minutes. The gas employed in the plasma-treatment can additionally comprise an inert gas such as argon. The plasma treatment time is preferably at a flow rate of 50 to 500 sccm (standard cubic centimeters). The thickness of the surface treatment is sensitive to plasma flow rate and chamber temperature, as will be understood by the skilled artisan. Since the coating is dependent on a number of variables, the optimal variables for obtaining the desired or optimal coating may require some adjustment. If one parameter is adjusted, a compensatory adjustment of one or

more other parameters may be appropriate, so that some routine trial and error experiments and iterations thereof may be necessary in order to achieve the coating according to the present invention. However, such adjustment of process parameters, in light of the present disclosure and the state of the art in plasma treatment, should not involve undue experimentation. As indicated above, general relationships among process parameters are known by the skilled artisan, and the art of plasma-treatment has become well developed in recent years. The Examples below provide the Applicants' best mode for forming the coating on a highly fluorinated RGP lens.

The contact lenses of the present invention are especially advantageous for extended-wear or specialty uses, such as for relatively thick lenses. Extended wear lenses are lenses capable of being worn overnight, preferably capable of being worn for at least one week, most preferably capable of wear for a continuous period of one week to one month. By "capable," is meant lenses approved by one or more governmental regulatory authorities for such consumer use, for example, the U.S. Food & Drug Administration (USFDA) in the U.S. or its equivalent in other countries.

The Examples, which follow, are illustrative of specific embodiments of the invention, and various uses thereof. They are set forth for explanatory purposes only, and are not to be taken as limiting the invention.

EXAMPLE 1

A number of high-Dk fluoropolymeric contact lens articles were made according to the subject invention and are described below. Molded rods of the material were obtained from Random Technologies (San Francisco, California), which were made from Teflon AF 1600, comprising 65 mole percent PDD and 45 mole percent TFE, supplied by DuPont. The rods' dimensions were 12.7 mm diameter and 4 mm thick. Buttons were cut from the rods and lathed into contact lenses by techniques well known in the art. An exemplary contact lens exhibited the characteristics in Table 1 below.

TABLE 1

<u>Property</u>	<u>Teflon® AF lens*</u>
Rockwell Hardness	106
Flexural Modulus (MPa)	1100
O ₂ Permeability (Barrers)	260
T _g (°C)	164

* Teflon® AF is a registered trademark of E.I duPont de Nemours (Wilmington, DE)

EXAMPLE 2

This Example illustrates a process for the surface modification of a contact lens according to the present invention. High-Dk fluoropolymeric lenses made according to Example 1 above from Teflon® AF 1600 polymeric material were plasma treated as follows: The lenses were placed concave side up on an aluminum coated tray and the tray placed into a plasma treatment chamber. The plasma treatment chamber was a direct current DC RFGD chamber manufactured by Branson GaSronics Division (Model 7104). This chamber was a cold equilibrium planar configuration which had a maximum power of 500 watts. All lenses were prepumped to 0.01 torr prior to any plasma treatment from residual air in the chamber. This process reduced the relative treatment level of the

polymer by controlling gas pressure. The lens was first treated by passing hydrogen gas at 50 sccm into the chamber. The lenses were plasma treated for a period of 10 minutes (300 watts, 0.3 torr). Subsequently, the lenses were treated by passing air at 250 sccm into the chamber while plasma treating the lenses for a period of 5 minutes (100 watts, 0.3 torr). The contact angle of the lens with water (HPLC grade H₂O, 72.4 dynes/cm) was, before the plasma treatment, 115 degrees and, after the plasma treatment, was 0 degrees

Many other modifications and variations of the present invention are possible in light of the teachings herein. It is therefore understood that, within the scope of the claims, the present invention can be practiced other than as herein specifically described.

CLAIMS

We claim:

1. A high-Dk, fluoropolymeric, rigid gas-permeable contact lens-article, either a contact lens or a blank for lathing such a contact lens, made in bulk from a material comprising an amorphous copolymer of perfluoro-2,2-dimethyl-1,3-dioxole with one or more copolymerizably acceptable, ethylenically-unsaturated fluorinated comonomers, the proportion of perfluoro-2,2-dimethyl-1,3-dioxole in the copolymer being at least about 20 mole percent of the copolymer.

2. The contact lens article as set forth in claim 1, wherein the copolymer further comprises from 10 to 80 weight percent of one or more other comonomers selected from the group consisting of tetrafluoroethylene, hexafluoropropylene, chlorotrifluoroethylene, vinylidene fluoride, perfluoro(alkyl vinyl) ether having the formula $\text{CF}_2=\text{CFO}(\text{CF}_2\text{CFXO})_n\text{R}_f$, wherein X is F or CF_3 , n is 0-5, and R_f is a perfluoroalkyl group of 1-6 carbon atoms, carboxylic and sulfonic acid derivatives, and mixtures thereof.

3. The contact lens article of claim 1, wherein the article is a contact lens capable of providing refractive correction with a diopter range of -20.00D to $+20.00\text{D}$.

4. The contact lens article of claim 1, wherein the article is a contact lens that has been surface-treated to improve the wettability and comfort of the lens such that, relative to the bulk material, the surface of the lens, the surface has increased oxygen and/or nitrogen content.

5. The contact lens article of claim 1, wherein the copolymer comprises 25 to 75 mole percent of monomer units from tetrafluoroethylene.

6. The contact lens article of claim 5, wherein the total mole percent of any other monomer units in the copolymer, in addition to perfluoro-2,2-dimethyl-1,3-dioxole and tetrafluoroethylene, is less than the mole percent of tetrafluoroethylene.
7. The contact lens article of claim 1, wherein the copolymer comprises a copolymer of perfluoro-2,2-dimethyl-1,3-dioxole with tetrafluoroethylene.
8. The contact lens article as set forth in claim 1, wherein said material has a T_g greater than about 120°C.
9. The contact lens article as set forth in claim 1, wherein said material has a modulus of from about 1000 to 2500 MPa.
10. The contact lens article as set forth in claim 1, wherein said material has an oxygen permeability of about 100 to 1200.
11. The contact lens article as set forth in claim 1, wherein said polymer comprises 20 to 75 percent of monomeric units of perfluoro-2,2-dimethyl-1,3-dioxole.
12. A contact lens article as set forth in claim 1, wherein the copolymer further comprises from 5 to 25 weight percent of one or more other comonomers selected from the group consisting of hexafluoropropylene, chlorotrifluoroethylene, vinylidene fluoride, perfluoro(alkyl vinyl) ethers having the formula $CF_2=CF(O)(CF_2CFXO)_nR_f$, wherein X is F or CF_3 , n is 0-5, and R_f is a perfluoroalkyl group of 1-6 carbon atoms, carboxylic and sulfonic acid derivatives, and mixtures thereof.
13. The contact lens article as set forth in claim 1, wherein the article is a contact lens adaptable for use as an extended-wear lens.
14. The contact lens article of claim 13, wherein said lens is capable of a period of extended continuous contact in the eye of at least seven days.

15. A method for treating the surface of a fluorinated contact lens comprising an amorphous copolymer of perfluoro-2,2-dimethyl-1,3-dioxole with tetrafluoroethylene, comprising the following steps:

- (a) plasma-treating the lens with an hydrogen-containing atmosphere at a wattage of 100 to 1000 watts and a pressure of 0.1 to 1.0 torr, and
- (b) oxidizing the lens by plasma-treating the lens with an oxygen- or nitrogen-containing compound at a wattage of 25 to 1000 watts and a pressure of 0.1 to 1.0 torr.

16. The method of claim 15, wherein the plasma-treatment in step (a) is 200 to 500 watts for a period of 2 to 20 minutes.

17. A method of claim 15, wherein said copolymer comprises 20 to 75 mole percent of monomeric units of perfluoro-2,2-dimethyl-1,3-dioxole and 25 to 80 mole percent of monomeric units of tetrafluoroethylene.

18. The method of claim 15, further comprising the attachment of a hydrophilic polymer to the surface to the lens.

19. A method of making a fluorinated contact lens comprising an amorphous copolymer of perfluoro-2,2-dimethyl-1,3-dioxole, comprising the following steps:

- (a) molding the copolymer into a shaped article,
- (b) optionally cutting the article into smaller articles for the lathing of a contact lens,
- (c) lathing the article into the shape of a contact lens,
- (d) optionally polishing the lens and
- (e) surface-treating the lens to improve its wettability and biocompatibility.

20. The method of claim 19, wherein the surface treatment comprises treating the lens with an hydrogen-containing atmosphere for at least 2 minutes, at a wattage of 100 to 1000 watts and a pressure of 0.1 to 1.0 torr, and subsequently oxidizing the lens by plasma-treating the lens with an oxygen- or nitrogen-containing compound for at least 2 minutes, at a wattage of 25 to 1000 watts and a pressure of 0.1 to 1.0 torr, to produce an oxidized coating increased in oxygen and/or nitrogen content.

INTERNATIONAL SEARCH REPORT

Int. Application No
PCT/US 99/28144

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 G02B1/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 G02B C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 443 986 A (CIBA GEIGY AG) 28 August 1991 (1991-08-28) claims 1-24 page 2, line 24 - line 56 page 5, line 21 - line 30	1-14
P, A	EP 0 950 672 A (ASAHI GLASS CO LTD) 20 October 1999 (1999-10-20) claims 1-10 page 8, line 16 - line 28 page 9, line 21 - line 22 page 8	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

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- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/28144

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